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# The Palladium Catalyzed Nucleophilic Substitution of Aryl Halides by Thiolate Anions

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In the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium, phenyl and methyl or methoxyphenyl iodides and bromides were found to react with thiolate anions in alcoholic solvents, to give the corresponding aryl sulfides in excellent yield. The reaction is useful to prepare symmetrical or unsymmetrical diaryl sulfides and aryl alkyl sulfides. The reaction mechanism does not involve aryl halide radical anions, but is thought to involve oxidative addition of aryl halide to Pd(0), nucleophilic substitution on the adduct followed by reductive elimination.

Aryl halides which are not activated by electron withdrawing substituents are inert to the usual nucleophilic reagents. Under special conditions, however, such unactivated aryl halides undergo substitution of halogens by nucleophiles. Besides the reactions *via* aryne intermediates under conditions involving high temperature or very strong bases, there have been noticed two kinds of substitution: aromatic $S_{RN}1$ which are stimulated by the presence of good electron donors,$^{1)}$ and substitution catalyzed by the transition metal complexes.

As examples of the latter kind of reactions, there have been known that Pd(0) or Pd(II) catalyzes the substitution of aryl halides by cyanide,$^{2)}$ acetylide anions,$^{3)}$ $\pi$-nucleophiles,$^{4)}$ and other organometallic reagents.$^{5)}$ Ni(0) catalysts also promote the reaction with acetylide$^{3)}$ or other carbanions$^{6)}$ and halogen exchange with halide ions.$^{7)}$

As preliminarily reported, it has been found that in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$, aryl bromides and iodides react easily with thiolate anions in dimethyl sulfoxide (DMSO) to give aryl sulfides in satisfactory yield.$^{8)}$ Recently, similar reaction of alkenyl halide also has been developed.$^{9)}$

$$ArX + RS^- \xrightarrow{Pd(PPh_3)_4} ArSR + X^-$$

X: I, Br and R: Ph, Alkyl

On the other hand, quite similar reaction of aryl halides with arenethiolates giving sulfides has been known to proceed without metal complexes, in liquid ammonia under irradiation of Pyrex-filtered light, and the $S_{RN}1$ mechanism was proposed for the reaction.$^{10)}$

The present paper described the results of a further survey on the chemistry of the Pd(0) catalyzed reaction giving sulfides, comparing with that of the $S_{RN}1$ reaction.

## Results

Table 1 shows the result of the reaction carried out by heating a solution of aryl halide (2 mmol), arene- or alkanethiol (2 mmol), sodium *t*-butoxide (4 mmol), and a catalytic amount of tetrakis(triphenylphosphine)palladium in a solvent, the yield of the sulfide being obtained by GLC analysis.

Table 1 apparently shows the catalytic effect of $Pd(PPh_3)_4$. Without the catalyst, PhI, $p$-$ClC_6H_4I$, $p$-$ClC_6H_4Br$, and $m$-$MeOC_6H_4I$ reacted with $PhS^-$ in DMSO to give low yield of the corresponding sulfides, and *p*-methyl and *p*-methoxy derivatives scarecely reacted and the aryl halides remained in the mixture under the same conditions. However, the presence of $Pd(PPh_3)_4$ in the reaction mixture converted all aryl halides into the corresponding sulfides in high yield. Palladium acetate also promotes the reaction, but seems inferior to $Pd(PPh_3)_4$ in the catalytic efficiency. Yield of diphenyl sulfide in the reaction of iodo benzene and $PhS^-$ was still lower than that in the $Pd(PPh_3)_4$ catalyzed reaction, even when 10 mol% of $Pd(OAc)_2$ was present.

In preliminary experiments,$^{8)}$ DMSO was chosen as a solvent, since in such an aprotic solvent nucleophile such as thiolate anion was considered to be more reactive than in a protic solvent. However, the results of the reaction of iodobenzene with benzenethiolate ion carried out in various easily available solvents indicate that alcohols are the most recommendable solvents.

Thus, the reaction in refluxing ethanol gave diphenyl sulfide in almost quantitative yield even in the presence of only 1 mol% of the catalyst, $Pd(PPh_3)_4$.

For preparative scale, it is most convenient to reflux a mixture made by adding aryl halide, thiol and then 1 mol% of $Pd(PPh_3)_4$ to a solution of sodium alcoholate prepared by dissolving sodium metal in the alcoholic solvent (see Experimental part). For the reaction of aryl iodide in ethanol, 4 h refluxing is sufficient to complete the reaction. Starting from iodobenzene (50 mmol), diphenyl sulfide and phenyl *t*-butyl sulfide were isolated in 88 and 65% yield, respectively.

Table 1 shows that the reaction proceeds with not only iodobenzene and its methyl or methoxy derivatives, but also with the corresponding unactivated aryl bromides. Aryl bromides react more slowly than aryl iodides. Thus, the reaction of bromobenzene in refluxing ethanol under which iodobenzene reacted smoothly, gave the sulfide only in low yield, but gave the excellent results under the conditions of refluxing alcohol of higher boiling point, *n*-BuOH.

Aryl chlorides are poor substrates toward the Pd(0) catalyzed substitution. Chlorobenzene was converted into the sulfide in only a trace amount under the same conditions. Chloronaphthalene and $EtS^-$ gave a mod-

TABLE 1. $Pd(PPh_3)_4$ CATALYZED SULFENYLATION OF ARYL HALIDE

| Run | ArX | Thiol | $Pd(PPh_3)_4$ | Solvent | Temp/°C | Sulfide Yield/% |
|---|---|---|---|---|---|---|
| 1 | $C_6H_5I$ | PhSH | — | DMSO | 100 | 22 (94) |
| 2 | | | 0.08 | DMSO | 100 | 75 |
| 3 | | | 0.08 | DMSO | 100 | 83 |
| 4 | | | 0.08 | DMF | 100 | 59 |
| 5 | | | 0.08 | $CH_3CN$ | reflux | 11 |
| 6 | | | 0.08 | *n*-BuOH | reflux | 100 |
| 7 | | | 0.08 | EtOH | reflux | 100 |
| 8 | | | — | EtOH | reflux | 0 |
| 9 | | | 0.02 | EtOH | reflux | 97 |
| 10 | $C_6H_5I$ | *t*-BuSH | 0.08 | EtOH | reflux | 100 |
| 11 | $C_6H_5I$ | *n*-BuSH | 0.08 | EtOH | reflux | 42 |
| 12 | | | 0.08 | *n*-BuOH | reflux | 90 |
| 13 | $C_6H_5I$ | EtSH | 0.08 | *n*-BuOH | reflux | 66 |
| 14 | *p*-$CH_3C_6H_4I$ | PhSH | — | DMSO | 100 | 0 |
| 15 | | | 0.08 | DMSO | 100 | 78 |
| 16 | | | 0.02 | EtOH | reflux | 85 |
| 17 | *m*-$CH_3C_6H_4I$ | PhSH | 0.02 | EtOH | reflux | 85 (81) |
| 18 | *o*-$CH_3C_6H_4I$ | PhSH | 0.02 | EtOH | reflux | 98 (72) |
| 19 | *p*-$CH_3OC_6H_4I$ | PhSH | — | DMSO | 100 | 6 |
| 20 | | | 0.08 | DMSO | 100 | 78 (76) |
| 21 | | | 0.02 | EtOH | reflux | 91 |
| 22 | *m*-$CH_3OC_6H_4I$ | PhSH | — | DMSO | 100 | 22 (88) |
| 23 | | | 0.08 | DMSO | 100 | 83 |
| 24 | | | 0.02 | EtOH | reflux | 100 |
| 25 | *o*-$CH_3OC_6H_4I$ | PhSH | 0.02 | EtOH | reflux | 65 |
| 26 | *p*-$ClC_6H_4I$ | PhSH | — | DMSO | 100 | 33 |
| 27 | | | 0.08 | DMSO | 100 | 79 |
| 28 | | | 0.02 | EtOH | reflux | 70 |
| 29 | 2,6-$Me_2C_6H_3I$ | PhSH | 0.02 | EtOH | reflux | 16 (19) |
| 30 | PhBr | PhSH | — | DMSO | 100 | 7 (23) |
| 31 | | | 0.08 | DMSO | 100 | 82 |
| 32 | | | 0.08 | EtOH | reflux | 19 |
| 33 | | | 0.08 | *n*-BuOH | reflux | 100 |
| 34 | *p*-$MeC_6H_4Br$ | PhSH | — | DMSO | 100 | 4 |
| 35 | | | 0.08 | DMSO | 100 | 51 |
| 36 | | | 0.08 | *n*-BuOH | reflux | 100 |
| 37 | *p*-$MeOC_6H_4Br$ | PhSH | — | DMSO | 100 | 3 |
| 38 | | | 0.08 | DMSO | 100 | 52 |
| 39 | | | 0.08 | *n*-BuOH | reflux | 80 |
| 40 | *p*-$ClC_6H_4Br$ | PhSH | — | DMSO | 100 | 28 |
| 41 | | | 0.08 | DMSO | 100 | 59 |
| 42 | PhCl | PhSH | 0.08 | DMSO | 100 | trace |
| 43 | α-NaPhCl | EtSH | 0.08 | DMSO | 100 | 46 |
| 44 | | | — | DMSO | 100 | 38 |

ArX: 2 mmol, thiol: 2 mmol, *t*-BuONa: 4 mmol, solvent: 20 ml.

erate yield of the sulfide, but the almost same results were obtained even without a catalyst.

As shown in Table 2 a), competitive experiments using large excess of substituted iodobenzenes showed somewhat retarding effects of the electron repelling substituents ($\rho \fallingdotseq +1.0$).

Alkanethiolates such as $EtS^-$, *n*-$BuS^-$, and *t*-$BuS^-$ are also good substituting reagents. Semiquantitative competitive experiment on the reaction of iodobenzene with excess of a mixture of $PhS^-$ and *t*-$BuS^-$ showed *t*-$BuS^-$ reacts about 9 times faster than $PhS^-$ as shown in Table 2 b).

## Discussion

The reactions of aryl iodides and bromides with thiolate anions in the presence of $Pd(PPh_3)_4$ were found to be useful for preparation of unsymmetrical diaryl or aryl alkyl sulfides. It should be noteworthy that the reaction can be applied to the aryl halides bearing electron repelling substituents.

The reaction needs no peculiar solvents, but the

Table 2. Competitive reaction

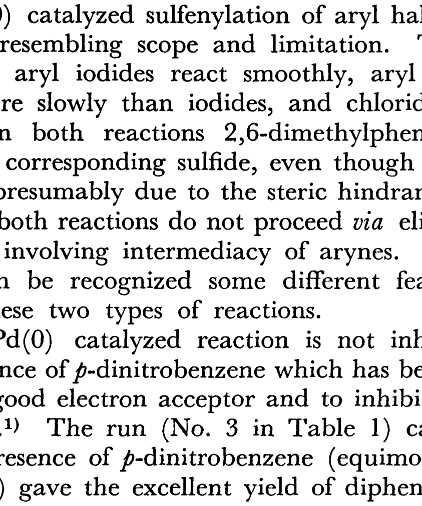
| | | | | |
|---|---|---|---|---|
| a) Reaction of $PhS^-$ with PhI and $XC_6H_4I$ | | | | |
| X | $[PhI]_i/[XC_6H_4I]_i$ | | $[XC_6H_4SPh]_f/[C_6H_5SPh]_f$ | Relative rate $k_X/k_H$ |
| $p$-Cl | 1.00 | | 1.80 | 1.8 |
| $p$-$CH_3$ | 1.00 | | 0.79 | 0.8 |
| $p$-$CH_3O$ | 1.00 | | 0.60 | 0.6 |
| b) Reaction of PhI with $PhS^-$ and $t$-$BuS^-$ | | | | |
| $[PhSH]_i$ | $[t\text{-}BuSH]_i$ | $[PhSPh]_f$ | $[t\text{-}BuSPh]_f$ | Relative rate $k_{t\text{-}BuS^-}/k_{PhS^-}$ |
| 4.92 | 2.01 | 0.18 | 0.63 | 10.2 |
| 9.84 | 2.00 | 0.20 | 0.36 | 8.7 |
| c) Reaction of $PhPdI(PPh_3)_2$ with $PhS^-$ and $t$-$BuS^-$ | | | | |
| $[PhSH]_i$ | $[t\text{-}BuSH]_i$ | $[PhSPh]_f$ | $[t\text{-}BuSPh]_f$ | Relative rate $k_{t\text{-}BuS^-}/k_{PhS^-}$ |
| 5.06 | 1.04 | 0.18 | 0.25 | 8.0 |

most common solvents, alcohols. Reaction temperature can be regulated by choosing the alcholic solvents depending on the reactivity of substrate. Thus, aryl iodides and bromides react smoothly in refluxing ethanol and 1-butanol, respectively. Work-up for separation of the products is reasonably easy as shown in the experimental part.

It is interesting to compare the features between the present reaction and the sulfenylation of unactivated aryl iodide proceeding through $S_{RN}1$ processes developed by Bunnett and Creary. At first glance on Table 1 in which yields of the sulfide produced through the $S_{RN}1$ is noted in parentheses, both the $S_{RN}1$ and the Pd(0) catalyzed sulfenylation of aryl halides seem to have resembling scope and limitation. Thus, unactivated aryl iodides react smoothly, aryl bromides react more slowly than iodides, and chlorides hardly react. In both reactions 2,6-dimethylphenyl iodide gave the corresponding sulfide, even though the yields are low presumably due to the steric hindrance, showing that both reactions do not proceed *via* elimination-addition involving intermediacy of arynes. However, there can be recognized some different features between these two types of reactions.

The Pd(0) catalyzed reaction is not inhibited by the presence of *p*-dinitrobenzene which has been known to be a good electron acceptor and to inhibit the $S_{RN}1$ processes.[1] The run (No. 3 in Table 1) carried out in the presence of *p*-dinitrobenzene (equimolar to the substrate) gave the excellent yield of diphenyl sulfide.

Secondly, the $S_{RN}1$ reactions of chlorophenyl iodides or bromides with $PhS^-$ give almost exclusively disulfenylated products,[10] but in the Pd(0) catalyzed reaction, monosulfenylated products $ClC_6H_4SPh$ are predominantly formed, even if excess of thiolate is used.



Inhibition by an electron acceptor, and disulfenylation of chlorophenyl halides are the striking features which strongly support the $S_{RN}1$ mechanism involving electron transfer to aryl halides giving anion radicals. Consequently, the present reaction lacking these features should be essentially different from the $S_{RN}1$ reaction, and not involving radical anions.

The most plausible mechanism of the Pd(0) catalyzed sulfenylation involves oxidative addition of aryl halide to Pd(0), followed by nucleophilic attack of thiolate anion on the adduct.

$$\mathrm{Ar\text{-}X} + \mathrm{Pd(0)} \longrightarrow \mathrm{Ar\text{-}Pd\text{-}X}$$
$$\mathrm{RS^-} + \mathrm{ArPdX} \longrightarrow \mathrm{ArSR} + \mathrm{Pd(0)} + \mathrm{X^-}$$

It has been established that aryl halide adds to $Pd(PPh_3)_4$ to give halo(aryl)bis(triphenylphosphine)-palladium(II), $ArPdX(PPh_3)_2$ in high yield.[11] The observed tendency of the substituent effects in the present reaction ($\rho \fallingdotseq 1.0$) concords with the qualitative observation of the substituent effects in the oxidative addition.[11] Then it is quite natural to consider the oxidative addition as the first step of the Pd(0) catalyzed reaction of aryl halide.

Actually, treatment of iodo(phenyl)bis(triphenylphosphine)palladium(II) prepared by the method of Fitton *et al.*[11] with a solution of $PhS^-$ gave diphenyl sulfide almost quantitatively. Furthermore, competitive reaction of the adduct with excess amounts of $PhS^-$ and $t$-$BuS^-$ showed that $t$-$BuS^-$ reacted about 8 times faster than $PhS^-$. This is in tolerable agreement with the result of the competitive reaction of iodobenzene with $PhS^-$ and $t$-$BuS^-$ described above. These facts strongly suggest intermediacy of the oxidative adducts between Pd(0) and aryl halide.

By the way, a mechanism involving an electron transfer to give anion radicals $ArX^{\overline{\cdot}}$ has been suggested as a initial step in the oxidative addition.[12] This possibility, however, seems unlikely at least in the addition of aryl halide to the Pd(0), because the Pd(0) catalyzed reaction of aryl halide with thiolate anion cannot be considered to involve generation of a radical anion, $ArX^{\overline{\cdot}}$. The anion radical once formed, would propagage $S_{RN}1$ reaction, which could show the features different from the present reaction, as discussed above.

The initial step of the reaction between the oxidative adduct and thiolate anion is thought to be a nucleophilic substitution on the palladium atom in the adduct. And reductive elimination on the substituted product may give aryl sulfide, regenerating Pd(0). Besides

$$\mathrm{ArPd\text{-}X} + \mathrm{SR^-} \longrightarrow \mathrm{Ar\text{-}Pd\text{-}SR} + \mathrm{X^-}$$

$$\text{Ar-Pd-SR} \longrightarrow \text{ArSR} + \text{Pd(0)}$$

thiolate and cyanide anions, triphenylphosphine also was found to react with the unactivated aryl halides in the presence of the Pd(0) catalyst, giving aryltriphenylphosphonium salts in high yield, as shown in Table 3.

TABLE 3. $Pd(PPh_3)_4$ CATALYZED REACTION OF ARYL HALIDE WITH $PPh_3$

| ArX | Product isolated yield/% | $ArP^+Ph_3X^-$ Mp/°C | Mp(lit)[a)]/°C |
|---|---|---|---|
| PhI | 93 | 325—328 | 328—326 |
| $p$-$MeC_6H_4I$ | 80 | 208—209 | 207—209 |
| $p$-$MeOC_6H_4I$ | 93 | 217—218 | 217—218 |
| PhBr | 7 | 286—288 | 288 |

ArX: 2 mm, $PPh_3$: 2 mmol, $Pd(PPh_3)_4$: 0.08 mmol, solvent: benzene: 3 ml.

a) L. Horner and H. Hoffman, *Chem. Ber.*, **91**, 45 (1958).

These three soft nucleophiles have been found to be particularly reactive toward the platinum atom of *trans*-$[Pt(py)_2Cl_2]$.[13)] On the other hand, the Pd(0) catalyzed substitution of aryl halide by hard nucleophiles, for example, alkoxide and various types of carbanions such as $\overset{-}{C}H_2CN$, $\overset{-}{C}H(COOR)_2$, *etc.* was unsuccessful. These tendencies may be compatible with the mechanism involving nucleophilic attack on the palladium atom.

## Experimental

All reagents were commercially available and, of reagent-grade quality, unless otherwise noted. Tetrakis(triphenylphosphine)palladium(0) was prepared according to the literature.[14)] Reaction products, sulfides and phosphonium salts were identified by comparing their IR spectra with those of the authentic samples. GLC analysis was performed with a Ohkura model 710 gas chromatograph.

*Reactions with Thiolate.* *Small Scale Experiment*: A solution of aryl halide (2 mmol), thiol (2 mmol), sodium *t*-butoxide (4 mmol), and 1—4% molar amount of $Pd(PPh_3)_4$ in a solvent (20 ml) was heated at 100 °C or boiling points of solvents under a nitrogen stream with stirring. For the reactions of aryl iodides, reactions complete after 3 h, but prolonged heating does not affect yield of the sulfides. It takes more than 10 h to complete the reaction of aryl bromides. Yields of the products were determined by GLC analysis. The results (reaction time: 18 h) are shown in Table 1.

*Preparative Scale Experiment*: In a three necked flask (500 ml), a solution of sodium ethoxide was prepared by stirring a mixture of ethanol (200 ml) and sodium (3 g) for 30 min under nitrogen. To the solution was added a solution of iodobenzene (50 mmol) and thiophenol (50 mmol) in ethanol (50 ml), and then $Pd(PPh_3)_4$ (0.5 mmol). After refluxing the solution for 4 h with stirring, ethanol was driven off with a rotary evaporator. From the residue the product was extracted into pentane. After washing with water, usual work-up and distillation gave diphenyl sulfide (110—113 °C/5 mmHg) in 88% yield. Similarly the reaction with *t*-butyl mercaptane afforded *t*-butyl phenyl sulfide (85—90 °C/20 mmHg) in 65% yield.

*Reaction with Triphenylphosphine.* A solution of aryl iodide (2 mmol), triphenylphosphine (2 mmol), and $Pd(PPh_3)_4$ (0.08 mmol) in benzene (3 ml) was placed in a reaction tube. The tube was evacuated and sealed, and then immersed in a bath heated at 100 °C. After 18 h, aryl triphenylphosphonium salt crystallized from the mixture was filtered and washed with benzene. Yield and melting point observed are shown in Table 3.

*Competitive Reactions.* *Reactions of $PhS^-$ with Large Excess of Aryl Iodides*: An equimolar mixture of iodobenzene (15 mmol) and substituted iodobenzene (15 mmol) was allowed to react with thiophenol (1 mmol) in the presence of alkoxide (2 mmol) and $Pd(PPh_3)_4$ (0.02 mmol) in ethanol (30 ml) at 100 °C for 18 h. From the molar ratio of the produced sulfides relative reactivity of the aryl iodide, $k_{ArI}/k_{PhI}$ was estimated by the following equation.

$$k_{ArI}/k_{PhI} = [ArSPh]_f/[PhSPh]_f$$

*Reaction of PhI with $PhS^-$ and* t-*$BuS^-$*: A solution of iodobenzene (0.5—1.0 mmol), thiophenol (5—10 mmol), 2-methyl-2-propanethiol (2 mmol), alkoxide (20 mmol), and $Pd(PPh_3)_4$ (0.02 mmol) in ethanol (20 ml) was refluxed for 1 h. Amounts of the produced sulfides were determined by GLC method. The relative reactivity $k_{t\text{-BuS}^-}/k_{PhS^-}$ was calculated by the following equation,

$$\frac{k_{t\text{-BuS}^-}}{k_{PhS^-}} = \log\frac{[t\text{-BuSH}]_i - [t\text{-BuSPh}]_f}{[t\text{-BuSH}]_i} \Bigg/ \log\frac{[PhSH]_i - [Ph_2S]_f}{[PhSH]_i}$$

where the suffixes i and f indicate the initial and final concentrations, respectively.

*Reaction of $PhPdI(PPh_3)_2$ with $PhS^-$ and* t-*$BuS^-$*: Instead of iodobenzene and $Pd(PPh_3)_4$ in the above competitive experiment, $PhPdI(PPh_3)_2$ (0.5 mmol) was used.

The results of these competitive reactions were summarized in Table 2.

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